

Synthesis of visible-light active TiO₂ photocatalyst with Pt-modification: Role of TiO₂ substrate for high photocatalytic activity

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Abstract

Nano-sized TiO₂ photocatalysts were prepared by hydrolysis of TiCl₄ followed by calcination at different temperatures. X-ray diffraction (XRD) measurements revealed that all TiO₂ powders crystallized in rutile even before calcination. The photocatalytic activity of the raw TiO₂ powder clearly decreased with increasing calcination temperature. Pt-modification of the surface of TiO₂ increased photocatalytic activity under visible-light irradiation, depending on the calcination temperature. Maximal photocatalytic activity was obtained at calcination temperatures of 300–450 °C, which was correlated with the light absorption properties of the Pt complex on TiO₂ nano-particles. It was found that TiO₂ surface structure plays an important role in the formation of Ti–O–Pt bonds, resulting in a large visible-light absorbance and high photocatalytic activity under visible-light irradiation.

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1. Introduction

Recently TiO₂ photocatalysts have been utilized successfully in various fields such as air-purification, deodorizing, sterilization and self-cleaning [1,2]. However, a major problem encountered is that TiO₂ does not work as a photocatalyst with visible light. Therefore, the development of a TiO₂ photocatalyst that works efficiently under visible-light irradiation has attracted much attention over the past several years.

For the improvement of photocatalytic activity at $\lambda > 400$ nm, several types of photocatalysts have been proposed, for example, transition metal ion implanted TiO₂ [3,4], reduced TiO₂ [5], dye-sensitized TiO₂ [6–9], anion doped TiO₂ [10–15] and Pt-modified TiO₂. Among these, nitrogen doped TiO₂ and Pt-modified TiO₂ are expected to become commercially promising photocatalysts due to their high activity.

The effect of Pt compounds on photocatalytic activity under visible-light irradiation has been studied by several research groups. Kisch and co-workers investigated the photodegrada-

tion of 4-chlorophenol in aqueous solution using TiO₂ modified with a chloride complex of Pt [16–20]. Kim et al. reported that Pt-ion doped TiO₂ exhibited selective photocatalytic activity for chlorinated organic compounds [21]. Although the basic reaction mechanism of Pt-modified TiO₂ was proposed in these studies, little attention has been paid to the interaction between Pt compounds and its base TiO₂.

In our recent paper [22], we reported an innovative approach to modifying Pt complexes with different ligand structures on TiO₂ particles. The visible-light-induced photocatalytic activity was found to depend on the amount of Pt, but not greatly on the coordination number of Cl ions. However, the influence of base TiO₂ on the photocatalytic activity has not been completely elucidated.

In order to clarify the role of base TiO₂ in a Pt-modified TiO₂ photocatalyst, we prepared a series of rutile TiO₂ samples by hydrolysis of TiCl₄ followed by a heat treatment. TiO₂ samples were surface-treated with H₂PtCl₆·6H₂O, and their photocatalytic activity under visible-light irradiation was evaluated from decomposition of acetaldehyde in the gas phase. The influence of the calcination temperature of the base TiO₂ on light absorbance in the visible region and on photocatalytic activity was investigated.

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2. Experimental

2.1. Chemicals

An aqueous solution of titanium tetrachloride (TiCl_4 , purity > 99.9%) was provided from Ishihara Sangyo Kaisha, LTD. Chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was obtained from Ishihaku Kinzoku Kogyo Co. Inc. and used without further purification. The hypophosphorous acid and sodium hydroxide used were reagent grade and were obtained from Kanto Chemical Co. Inc.

2.2. Preparation of Pt-modified TiO_2

TiCl_4 solution at a concentration of 200 g/l expressed as TiO_2 was added dropwise to NaOH solution (20%) with stirring. After aging at 80 °C for 60 min, the solution was adjusted to pH 7 with 20% NaOH solution. Then, the slurry was filtered, washed and dried at 105 °C. The resulting powder was calcined at various temperatures before Pt-modification. Pt-modification of the surface of TiO_2 was carried out as follows: 50 g of TiO_2 was dispersed into 500 ml of aqueous solution of 0.027% $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Pt: TiO_2 (w/w) = 0.1:100). Into the dispersion, 0.75 ml of H_3PO_2 was added and the dispersion was aged at 90 °C for 60 min. Then the solution was adjusted to pH 7 with 20% NaOH solution. After neutralization, the Pt-modified TiO_2 was filtered, washed and dried at 105 °C.

2.3. Characterization

The crystal structure of the powders was studied by X-ray diffraction on a diffractometer (Rigaku Model Rint-2200) with Cu $K\alpha$ radiation. The crystallite size of the powders was estimated from X-ray line broadening. Specific surface areas were determined by the Brunauer–Emmet–Teller method. The diffuse reflective UV–vis spectra of the powders were measured using a Hitachi U-3300 spectrometer equipped with a diffuse reflectance attachment and transformed to a magnitude proportional to the extinction coefficient (K) through the Kubelka–Munk function. The composition of the powder was determined by X-ray fluorescence analysis using an X-ray spectrometer (Rigaku Model RIX-3000). The FT-IR absorption spectra were measured by a FT-IR spectrometer (JASCO FT/IR-610) equipped with a MCT detector. The sample cell was connected to a high vacuum (10^{-3} Torr; 1 Torr = 133.33 Pa) and was kept at 90 °C to eliminate the physically adsorbed water.

2.4. Photocatalytic reaction

Photocatalytic activity was evaluated by measuring the decomposition rate of acetaldehyde in a closed circulating type reactor. The reactor consists of a quartz vessel (800 cm^3) for photocatalytic reaction, flexible bag (2000 cm^3) and circulating pump. The initial concentration of acetaldehyde was 150 ppm, and the rate of gas circulation was 3 ml/min. The TiO_2 sample in the reactor was irradiated with a black fluorescent light

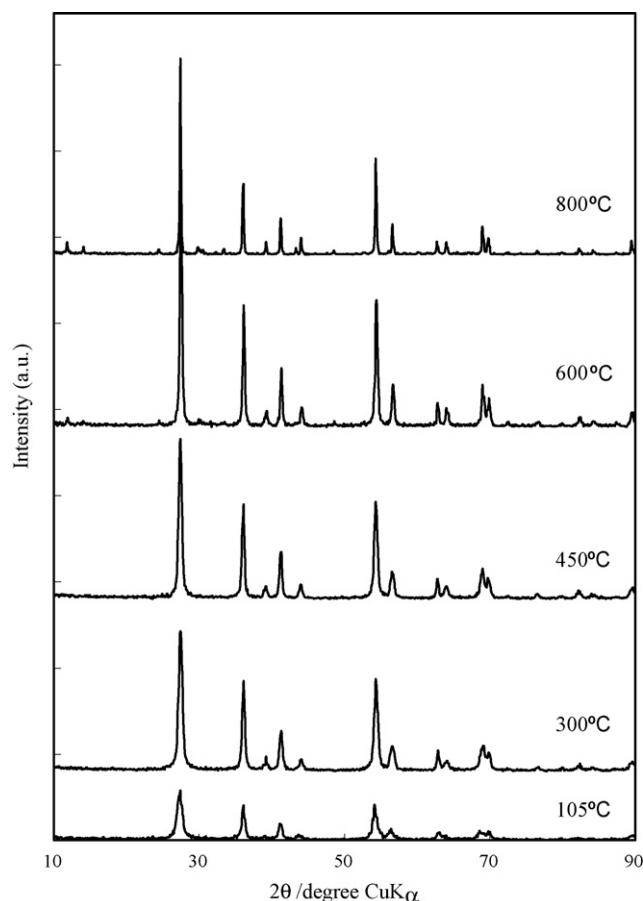


Fig. 1. XRD patterns of TiO_2 samples calcined at various temperatures.

(Matsushita Electric Model FL20SBL-B) and a white fluorescent light (Toshiba Model FL20SS-W). The illumination intensity at the surface of the sample was 0.5 mW/cm^2 for UV and 5700 lux for visible light. The light irradiation was started after the injected acetaldehyde reached a steady state in the reactor (30 min after injection). The concentration of acetaldehyde in the reactor was measured every 15 min by using gas chromatography (Hewlett Packard 5890 series II).

3. Results and discussion

3.1. Characterization of base TiO_2

Fig. 1 shows the XRD patterns of TiO_2 samples calcined at various temperatures (300–800 °C) before Pt-modification. The observed peaks can be attributed to the rutile phase even for uncalcined TiO_2 , and there appeared to be no peaks for anatase. The diffraction peaks corresponding to the rutile phase became sharp and strong with increased calcination temperature.

The crystallite size of powders was determined from the broadening of corresponding X-ray diffraction peaks by using Scherrer's formula $D = \kappa\lambda/\beta\cos\theta$, where λ is the wavelength of the X-ray radiation ($\lambda = 0.15418$ nm), κ is the Scherrer constant ($\kappa = 0.9$), θ is X-ray diffraction angle and β is the full-width at half-maximum (FWHM) of the (1 1 0) plane (in radians). These results are listed in Table 1. The calculated crystallite size of

Table 1

Crystallite size, BET surface area and photocatalytic reaction rate constant of the base TiO₂ samples prepared at various calcination temperatures

Temperature (°C)	Crystallite size (nm)	BET surface area (m ² /g)	Reaction rate constant (1/h)
105	11	125	2.4
300	14	68	1.6
450	18	53	0.8
600	24	32	0.5
800	45	9	0.3

TiO₂ prepared by drying at 105 °C was 11.0 nm and the size increased from 14.4 to 45.3 nm with increasing calcination temperature.

Zhang and Banfield [23] found that when particle size decreases sufficiently (smaller than ca. 14 nm), the total free energy of rutile is higher than that of anatase, and anatase becomes the stable phase. However, no peaks corresponding to anatase were observed in the TiO₂ samples prepared by the present synthesis procedure.

The specific surface area of the TiO₂ powders is also shown in Table 1. The sample without a calcination process had large surface area (125.3 m²/g), whereas it was markedly diminished to 68 m²/g by calcination at 300 °C, and then gradually decreased with an increasing calcination temperature up to 800 °C. These results indicate that the crystallinity of the obtained rutile particles increases as the calcination temperature increases, along with crystal growth.

The photocatalytic activity of the base TiO₂ was estimated from the degradation of acetaldehyde under black fluorescent light irradiation. The variation in the concentration of acetaldehyde dependent upon light irradiation time is shown in Fig. 2. As the reaction followed mass transfer-controlled first-order kinetics in the present experimental conditions, we calculated the first-order rate constant for the degradation of acetaldehyde by means of a linear least-square fit.

The reaction rate constants of the TiO₂ powders are listed in Table 1. The TiO₂ sample without a calcination process exhibited the highest activity for the degradation of acetaldehyde in UV light. The reaction rate constant clearly decreased

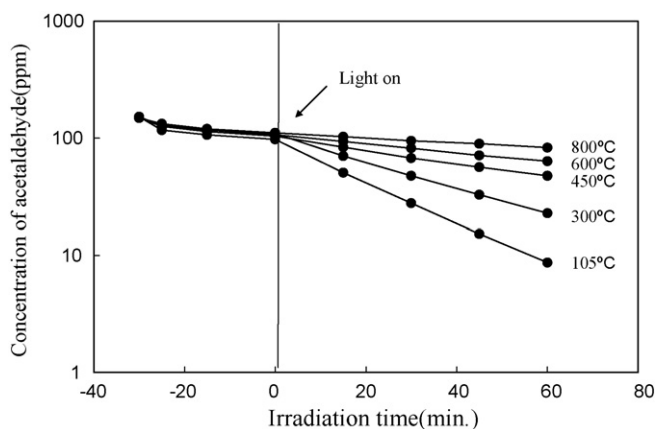


Fig. 2. Variation in the concentration of acetaldehyde upon light irradiation time.

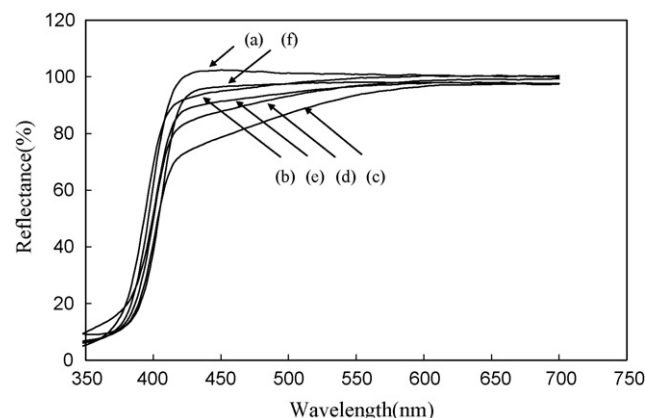


Fig. 3. Diffuse reflective UV–vis spectra of base TiO₂ (a), and Pt-modified TiO₂ prepared at different calcination temperatures (b–f). Calcination temperature: (b) 105 °C, (c) 300 °C, (d) 450 °C, (e) 600 °C, and (f) 800 °C.

with increasing calcination temperature, indicating that the photocatalytic activity depends strongly on the specific surface area. The increase in the crystallinity with increasing calcination temperature did not seem to affect photoactivity in this reaction system.

3.2. UV–vis spectrum

Fig. 3 shows the diffuse reflective UV–vis spectra of base TiO₂ and Pt-modified TiO₂ prepared at different calcination temperatures. The base TiO₂ had strong absorption only in the UV region corresponding to its band gap energy, while Pt-modified TiO₂ exhibited new absorption in the short wavelength region of visible light.

In order to investigate the visible-light absorption in detail, the Kubelka–Munk functions of Pt compounds were calculated from the differences in diffuse reflective spectra between Pt-modified TiO₂ and their base TiO₂. The results are shown in Fig. 4. Visible-light absorption was enhanced by the calcination of base TiO₂ at 300 °C before Pt-modification. However, absorption decreases with further increasing calcination temperature, and the sample calcined at 800 °C had very little absorption even with the same level of Pt content (Table 2). In

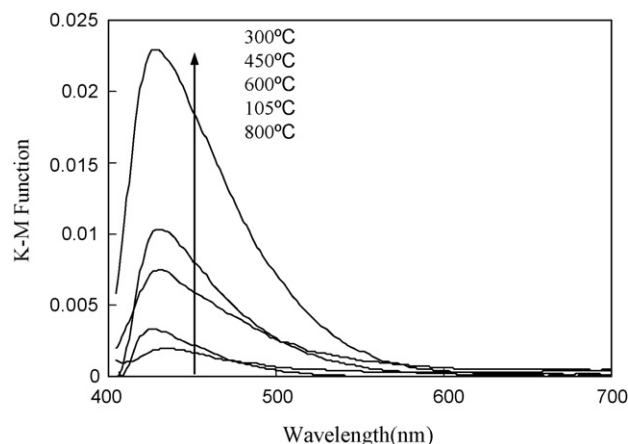


Fig. 4. Kubelka–Munk function of Pt compounds calculated from the difference in diffuse reflective spectra between Pt-modified TiO₂ and their base TiO₂.

Table 2
Pt and Cl content, and Cl/Pt atomic ratio of the Pt-modified TiO₂ samples

Temperature (°C)	Pt content (wt%)	Cl content (wt%)	Cl/Pt atomic ratio
105	0.100	0.070	1.4
300	0.105	0.037	0.7
450	0.104	0.045	0.9
600	0.104	0.017	0.3
800	0.102	–	0

addition, the absorption maxima in the visible-light region were slightly shifted to longer wavelengths with increasing calcination temperature. These results indicate that the interaction between Pt and TiO₂ was affected to a great extent by the surface condition of the TiO₂.

It is well known that the heat of immersion of TiO₂ in water has a maximum at a temperature of heat-treatment between 300 and 400 °C [24]. The heat of immersion depends on the amount of the water adsorbed per unit of surface area [25]. The calcination temperature of TiO₂ corresponding to the maximal visible-light absorption in the present study is roughly the same as the above temperature. These facts suggest that the optimum ligand structure of the Pt complex for visible-light absorption is related to the number of hydroxyl groups on the TiO₂ surface.

3.3. Photocatalytic activity under visible-light irradiation

The photocatalytic activity of Pt-modified TiO₂ samples was measured by the degradation of acetaldehyde under fluorescent lamp irradiation. The dependence of the reaction rate constant on the calcination temperature of the TiO₂ is shown in Fig. 5, along with the data for the sample without Pt-modification (105 °C). For comparison, the reaction rate constants of the base TiO₂ powders shown in Table 1 are also plotted. It can be seen that photocatalytic activity under fluorescent lamp

irradiation has been increased by Pt-modification, and that it is enhanced by the calcination of base TiO₂ up to around 450 °C. Further increases in calcination temperature, however, depressed photocatalytic activity. This temperature dependence is quite different from that associated with the original photocatalytic activity under UV light irradiation. In Fig. 5, the Kubelka–Munk function of Pt compound at 428 nm in each calcination temperature is also plotted. From this figure, it is concluded that the high photocatalytic activity under visible-light irradiation at about 300–450 °C is attributable mainly to visible-light absorption by the Pt compound.

Pt deposition on TiO₂ surface is well known to improve photocatalytic activity due to the retardation of electron–hole recombination [26]. In order to investigate the effect of Pt-modification on the photocatalytic activity under UV irradiation, the degradation of acetaldehyde under black fluorescent light was also measured. The results are plotted in Fig. 5. It is seen from this figure that the photocatalytic activity under UV light irradiation was increased by Pt-modification and that the reaction rate constant decreased monotonically with increasing calcination temperature. This temperature dependence is similar to that observed in the TiO₂ before Pt-modification. From these results, it could be assumed that Pt-modification in the present study also improves inherent photocatalytic activity of the base TiO₂ powders to some extent due to an efficient charge separation of the light generated electron–hole pairs.

3.4. Composition analysis and FT-IR absorption spectra

The photocatalytic activity of Pt-modified TiO₂ is affected by the structure of the chemisorbed Pt complex. We reported in a previous paper that Pt complexes containing at least one Cl ligand accelerated photocatalytic activity under visible-light irradiation [22]. The Cl content and the Cl/Pt atomic ratio in each sample are listed in Table 2. The Cl/Pt atomic ratio of the sample calcined at 300 and 450 °C are 0.7 and 0.9, respectively, indicating that these samples contain a certain quantity of ligand compositions corresponding to [PtCl(H₂O)₅]³⁺ or [PtCl(OH)₅]^{2–} [27]. Calcination at higher temperatures brought about a decrease in the Cl/Pt atomic ratio, and there was no detectable amount of Cl in the sample calcined at 800 °C.

In order to investigate the influence of calcination temperature on the nature of the TiO₂ surface, the FT-IR absorption spectra were measured for the samples before Pt-modification. Fig. 6 shows the FT-IR absorption spectra of base TiO₂ samples recorded in transmission mode as a function of calcining temperature. In this wavenumber range, a broad absorption band at 3600–3300 cm^{–1} and a sharp absorption band at 3700–3650 cm^{–1} were observed. The broad band centered at about 3400 cm^{–1} results from absorption by hydrogen-bonded surface species (hydroxyl and water), and the sharp band at 3700–3650 cm^{–1} is normally assigned to surface hydroxyl groups [28,29]. The spectra clearly showed the decrease of hydroxyl groups with increasing calcination temperature. In the case of TiO₂ treated at 800 °C, relatively scarce absorption in both wavenumber ranges, suggesting that the major portion of surface hydroxyl groups are disappeared.

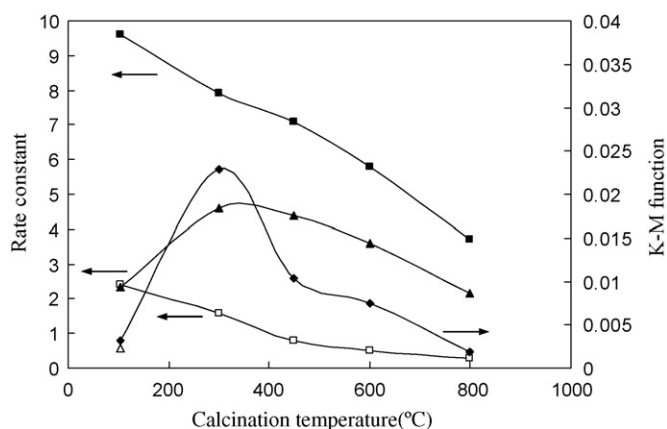


Fig. 5. Dependence of the reaction rate constant and K–M function on the calcination. (▲) Reaction rate constant of Pt-modified TiO₂ under fluorescent lamp irradiation, (△) reaction rate constant of base TiO₂ under fluorescent lamp irradiation, (□) reaction rate of base TiO₂ under UV irradiation, (◆) reaction rate of Pt-modified TiO₂ under UV irradiation, and (◆) K–M function of Pt compound at 428 nm.

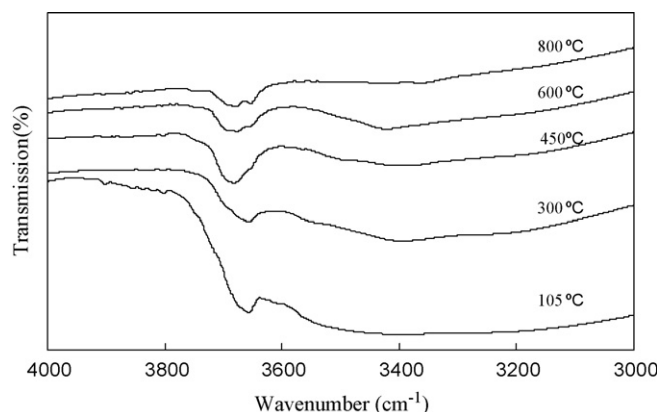


Fig. 6. FT-IR absorption spectra of base TiO₂ samples.

Morimoto et al. pointed out that number of hydroxyl groups on TiO₂ decreases with increasing temperature, and the remaining number of hydroxyl group is negligibly small at 800 °C [30,31]. Iwaki et al. also reported that when TiO₂ is pre-heated at high temperature, rehydration of surface titanium is retarded because of the stable rutile structure in the bulk and the stabilized oxo-groups on the surface [24]. In the present study, TiO₂ was calcined at various temperatures before Pt-modification. In the Pt-modification process, the calcined TiO₂ was immersed into an aqueous solution of H₂PtCl₆·6H₂O. The TiO₂ calcined at 800 °C was supposed to have a stable oxo-structure without a hydroxyl group, and it was not rehydrated even under wet conditions for the Pt-modification process. As a consequence, any Pt compound is not chemisorbed to the surface of the TiO₂ in the Pt-modification process.

In a previous paper [22], we suggested that Pt complexes were chemisorbed to the TiO₂ through Ti–O–Pt bonds. Ti–O–Pt bonding was also reported for [PtCl_x(H₂O)_{6-x}]^{4-x} ($x = 4-6$) [20] and for [Pt(bpy)](bpy = 2,2'-bipyridine) [32] complexes. These types of bonding are accompanied by a condensation reaction between the surface hydroxyl groups of the TiO₂ and Pt compounds. From these considerations, it was concluded that the surface hydroxyl groups of TiO₂ substrate have an important role for the chemisorption of Pt complexes. TiO₂ calcined at a temperature of around 300–450 °C has an optimum surface structure for the formation of Ti–O–Pt bonds, resulting in large visible-light absorbance and high photocatalytic activity under visible-light irradiation.

4. Conclusions

In this paper, we succeeded in developing a novel Pt-modified TiO₂ photocatalyst that shows significant activity in the degradation of acetaldehyde under visible-light irradiation. The synthesis procedure involved hydrolysis of TiCl₄, calcination and a Pt-modification process. The calcination temperature before the Pt-modification process greatly affected

absorbance in the visible region and photocatalytic activity. The optimum calcination temperature was around 300–450 °C, which was found to be related to the number of the hydroxyl groups per unit of surface area. Application of this Pt-modified TiO₂ photocatalyst shows promise in the fields of gas-phase reaction systems under visible-light irradiation.

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